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GAS-PHASE PHOTOCHEMICAL REACTIONS OF DODECAMETHYLCYCLOHEXASILANE WITH SILICON COMPOUNDS. KINETICS OF SOME INSERTION REACTIONS OF DIMETHYLSILYLENE

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Summary

Attempts to measure the kinetics of gas-phase insertion reactions of dimethylsilylene, generated by photolysis of dodecamethylcyclohexasilane, are described. Insertion of dimethylsilylene into silicon–hydrogen bonds was the main reaction with trimethylsilane, pentamethyldisilane, and *sym*-tetramethyldisilane; in all cases the activation energy for insertion was zero, and the rate constants were in the ratio of 1 : 3.1 : 4.3. Dimethylsilylene also inserted cleanly into hydrogen chloride with an activation energy of 28 kJ mol⁻¹. Photochemical reactions with methylchlorosilanes were much more complex, involving little or no silylene chemistry; such reactions as did occur appeared to proceed almost entirely by radical mechanisms.

Introduction

It is well known that pyrolysis of disilanes containing at least one silicon–hydrogen or silicon–chlorine bond does not proceed by a radical mechanism, but by formation of a silylene. During a kinetic study of the pyrolysis of pentamethyldisilane [1] it was found that first-order kinetic plots for the disappearance of pentamethyldisilane showed a temperature-dependent deviation from linearity, curving towards lower slopes (i.e. implying some back-reaction) beyond 7% decomposition at 620 K, but not until 20% decomposition at 699 K. Pyrolysis of pentamethylchlorodisilane and other chlorodisilanes behaved similarly [2], but gave linear plots to higher conversion than did pentamethyldisilane. In no case was a trisilane observed. These results were discussed [1,2]

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in terms of the following scheme:



Whilst no unique explanation of the results was possible from the available data, it was thought that the trisilane $\text{Me}_7\text{Si}_3\text{X}$ must be more unstable than the corresponding disilane (i.e. $k_{-2} > k_1$), but other possibilities were that reaction 3 was important, or even that $k_2 < k_{-1}$, perhaps because $E_2 > E_{-1}$. This last possibility seemed unlikely, but prompted us to attempt to measure activation energies for insertion reactions of dimethylsilylene. There is in any case a need for such quantitative information in silicon chemistry, there being as yet few estimates of activation energies for silylene insertions [3].

Experimental

1. Apparatus and procedure

In order to measure activation energies which are likely to be small, a photochemical source of dimethylsilylene is necessary. We used dodecamethylhexasilane, $(\text{Me}_2\text{Si})_6$, which is known to photolyse quite cleanly in solution to give dimethylsilylene [4,5], although its low volatility makes it less suitable for gas phase studies. Preliminary photolyses were carried out in a quartz cell housed in an electric furnace and attached to a vacuum line, with provision for direct sampling by GLC [1]. To analyse for products with a wide range of retention characteristics, a dual column system with changeover valve was used. Both columns were packed with 5% SE 300 on Chromosorb, one being 4 m and the other 60 cm long. Those parts of the vacuum line necessary for the transfer of $(\text{Me}_2\text{Si})_6$ were heated to ca. 415 K and were fitted with Whitey stainless steel/PTFE vacuum valves. The photolysis lamp was a Hanovia low pressure mercury arc in the form of a U-tube 60 cm long. This was mounted adjacent to the reaction cell inside the furnace, but arranged so that most of the lamp was outside the hot zone to avoid increasing the vapour pressure of mercury in the lamp during experiments at elevated temperature. The vapour pressure of $(\text{Me}_2\text{Si})_6$ was too low to be measured with confidence by a pressure transducer attached to the inlet of the reaction cell, so the reservoir of $(\text{Me}_2\text{Si})_6$ could be surrounded by a thermostatted heater at 400 K, to ensure that a consistent amount was added to the reaction cell in each experiment. Analysis by the built-in GLC was complemented by mass spectrometry (VG micromass MM16).

Whilst the above arrangement was convenient for preliminary studies, it was unsuitable for quantitative work because of the difficulties caused by the low volatility of dodecamethylcyclohexasilane. Accordingly all of the quantitative measurements quoted below were obtained from experiments in individual quartz tubes fitted with breakseals, with analysis by mass spectrometry.

2. Materials

$(\text{Me}_2\text{Si})_6$ was generously provided by Professor R. West, University of Madison, Wisconsin [4]. Trimethylsilane was obtained commercially (Pierce Chemical Co.), and pentamethyldisilane was prepared by standard methods [1].

Results

1. Preliminary experiments

Preliminary experiments on the gas-phase photolysis of $(\text{Me}_2\text{Si})_6$ alone, with analysis by GLC and mass spectrometry, gave evidence for some minor radical reactions as well as the main silylene-forming reaction [5] (under our conditions, successive elimination of dimethylsilylene occurs):



The minor products detected were dimethylsilane, trimethylsilane, and *sym*-tetramethyldisilane, indicating the presence of dimethylsilyl- and trimethylsilyl-radicals. Small amounts of hydrogen, with traces of methane, were also observed; these probably resulted from secondary decomposition of polymer deposited on the walls of the reaction vessel [6], as they could be produced by photolysing the "empty" cell. Only when significantly larger amounts of hydrogen or methane were formed are they reported as products below. Both trimethylsilane and pentamethyldisilane were photolytically stable in our apparatus.

2. Photolysis of $(\text{Me}_2\text{Si})_6$ in the presence of trimethylsilane

Fixed quantities (ca. 6 mmHg) of $(\text{Me}_2\text{Si})_6$ were photolysed in the presence of a substantial excess of trimethylsilane (40 mmHg) between 413 and 510 K, the photolysis time being kept constant at 30 min (throughout the temperature range, reaction was not complete by 30 min). Analysis by GLC showed that the main product was pentamethyldisilane, with heptamethyltrisilane ($\text{Me}_7\text{Si}_3\text{H}$) as the next most abundant product. Minor products were *sym*-tetramethyldisilane ($\text{Me}_4\text{Si}_2\text{H}_2$) and hexamethyltrisilane ($\text{Me}_6\text{Si}_3\text{H}_2$). There was probably also a little dimethylsilane, but it could not be properly resolved from the large peak due to undecomposed trimethylsilane. The partial pressures of $\text{Me}_5\text{Si}_2\text{H}$ and $\text{Me}_7\text{Si}_3\text{H}$ (in some experiments only) were calculated from peak heights and corrected to a standard temperature (428 K), giving the results in Table 1.

3. Photolysis of $(\text{Me}_2\text{Si})_6$ in the presence of pentamethyldisilane

These experiments were conducted similarly to those with trimethylsilane, but with a constant initial pressure of 20 mmHg of pentamethyldisilane; the temperature range was 417 to 513 K. The pentamethyldisilane was found to contain ca. 11% of $\text{Me}_4\text{Si}_2\text{H}_2$, but no attempt was made to remove this, as its presence could be turned to advantage, as will be seen below. The main products were $\text{Me}_7\text{Si}_3\text{H}$ and $\text{Me}_6\text{Si}_3\text{H}_2$, with small quantities of dimethylsilane and trimethylsilane. The yields of trisilanes, calculated as above, are in Table 2.

4. Photolysis of $(\text{Me}_2\text{Si})_6$ in the presence of trimethylchlorosilane

Similar experiments were attempted with trimethylchlorosilane, but little reaction was observed even after prolonged photolysis up to 723 K; attempts to study the kinetics of insertion of dimethylsilylene with chlorosilanes were therefore abandoned. However, thermally-produced dimethylsilylene is known to insert into hydrogen chloride to form dimethylchlorosilane [2], so this reaction system was studied.

TABLE 1
YIELDS FROM PHOTOLYSIS OF $(Me_2Si)_6$ IN Me_3SiH

T (K)	413	414.5	422.5	433.5	443	455	458	463.5	473	474	494	510	Mean value
Me_5Si_2H (mmHg)	2.00	1.97	2.16	2.18	2.33	1.91	2.08	2.12	2.15	1.99	2.15	2.14	2.10 ± 0.12
Me_5Si_2H/Me_7Si_3H	3.60					3.46				3.32	3.71	3.58	3.53 ± 0.15

TABLE 2
YIELDS FROM PHOTOLYSIS OF $(Me_2Si)_6$ IN " Me_5Si_2H "

T (K)	417	429.5	443	453	463	473	482	495	513	Mean value
Me_7Si_3H (mmHg)	3.36	3.43	3.16	3.59	3.32	3.57	3.19	3.55	3.41	3.40 ± 0.16
$Me_6Si_3H_2$ (mmHg)	0.59	0.60	0.54	0.62	0.55	0.65	0.53	0.57	0.58	0.58 ± 0.04

TABLE 3
YIELDS FROM PHOTOLYSIS OF $(Me_2Si)_6$ IN HCl

T (K)	423	432.5	438	444	451.5	453	462	468	478	498.5	532
Me_2SiHCl (mmHg)	1.17	1.39	2.40	3.60	3.60	4.00	6.00	5.80	9.40	8.60	9.40

5. Photolysis of $(Me_2Si)_6$ in the presence of hydrogen chloride

$(Me_2Si)_6$ was photolysed in the presence of 40 mmHg of hydrogen chloride between 423 and 532 K. The main product was dimethylchlorosilane; trimethylchlorosilane and probably dimethylchlorosilane were also observed in combined amounts not exceeding 20% of the dimethylchlorosilane formed. The yield of the main product is shown in Table 3.

In contrast to the constant results in Tables 1 and 2, formation of dimethylchlorosilane shows a temperature-dependence. An Arrhenius-type plot of $\log P(Me_2SiHCl)$ against reciprocal temperature gave a good straight line between 423 and 478 K, with a slope corresponding to $27.7 \pm 1.0 \text{ kJ mol}^{-1}$. The temperature-dependence levelled off above 478 K, as may be seen from Table 3.

6. Semi-quantitative studies with chlorosilanes

To try to gain some insight into the photochemical reactions between $(Me_2Si)_6$ and chlorosilanes, we carried out a series of semi-quantitative experiments in individual break-seal quartz tubes, with analysis by mass spectrometry. In these experiments Me_3SiCl , Me_2SiHCl , and $MeSiCH_2$ were each photolysed for 30 min at 488 K, alone and in the presence of a standard amount of $(Me_2Si)_6$. The results are summarised below.

(i) Me_3SiCl . Virtually no photolysis was observed.

(ii) $Me_3SiCl + (Me_2Si)_6$. A small amount of the expected silylene insertion product Me_5Si_2Cl was found, but the main products were Me_2SiHCl , $HMe_2SiSiMe_2H$, and Me_6Si_2 .

(iii) Me_2SiHCl . This chlorosilane, unlike Me_3SiCl , was photolysed to some extent, the main products being H_2 , Me_2SiCl_2 , $MeSiHCl_2$, $HMe_2SiSiMe_2H$, CH_4 , small quantities of HCl , and a trace of $HMe_2SiSiMe_2Cl$.

(iv) $Me_2SiHCl + (Me_2Si)_6$. Relative to (iii), considerably less H_2 and CH_4 were produced, more $HMe_2SiSiMe_2H$, about the same amount of HCl and Me_2SiCl_2 , but virtually no $MeSiHCl_2$. $HMe_2SiSiMe_2Cl$ was still a minor product, but more was formed than in (iii). There was also some Me_2SiH_2 , indicated by a strong 59^+ peak in the mass spectrum.

(v) $MeSiHCl_2$. Photolysis gave about as much H_2 as in (iii), but much more HCl . Other products were $MeSiCl_3$, $HSiCl_3$, and small quantities of CH_4 and $MeSiH_2Cl$. There were also some unidentified minor products, probably containing two silicon atoms per molecule.

(vi) $MeSiHCl_2 + (Me_2Si)_6$. Relative to (v), there was much less H_2 , HCl , CH_4 , and $MeSiCl_3$. Other products were Me_2SiHCl , $MeSiH_2Cl$, and probably $HMe_2SiSiMe_2H$. A small amount of $HMe_2SiSiMe_2Cl$ was found [ca. 10% of the $HMe_2SiSiMe_2Cl$ formed in (iv)].

There were significant amounts of undecomposed reactants in all of the above experiments.

Discussion

1. Photolysis of $(Me_2Si)_6$ in the presence of trimethylsilane

The main reactions were silylene insertions:





Reaction 3 is likely to occur to some extent, as it does in the pyrolysis of pentamethyldisilane [1].

There were also some minor radical reactions, resulting from the formation of $\text{Me}_2\dot{\text{S}}\text{iH}$ from $(\text{Me}_2\text{Si})_6$, either directly or following hydrogen abstraction by dimethylsilylene:



The occurrence of reaction 9 led to a third silylene insertion reaction, 10:



The conventional way of measuring rate constants for reactions involving intermediates, such as 5 and 6, is to set up competitive experiments in which the rate of the reaction of interest is measured over a range of temperature relative to the rate of a known reaction, as measured by product yields. In the absence of any known reference reaction of dimethylsilylene this method could not be used, but nevertheless some conclusions can be drawn from the results of our simple procedure of measuring the temperature-dependence of the yield of a characteristic product from a reaction mixture of constant composition, photolysed for a fixed time.

Steady-state analysis of reactions 3–6 gives:

$$\frac{d[\text{Me}_5\text{Si}_2\text{H}]}{dt} = \frac{I_{\text{abs}} \{k_5 [\text{Me}_3\text{SiH}] - k_6 [\text{Me}_5\text{Si}_2\text{H}]\}}{k_3 + k_5 [\text{Me}_3\text{SiH}] + k_6 [\text{Me}_5\text{Si}_2\text{H}]} \quad (i)$$

and

$$\frac{d[\text{Me}_7\text{Si}_3\text{H}]}{dt} = \frac{I_{\text{abs}} k_6 [\text{Me}_5\text{Si}_2\text{H}]}{k_3 + k_5 [\text{Me}_3\text{SiH}] + k_6 [\text{Me}_5\text{Si}_2\text{H}]} \quad (ii)$$

Since the absolute yields of $\text{Me}_5\text{Si}_2\text{H}$ and $\text{Me}_7\text{Si}_3\text{H}$ were independent of temperature within 6% (Table 1), it follows from (i) and independently from (ii) that $E_3 = E_5 = E_6$. An approximate estimate of the relative size of k_5 and k_6 can be made as follows. From the mean values in Table 1, 40 mmHg of Me_3SiH gave 2.1 mm $\text{Me}_5\text{Si}_2\text{H}$ and 0.6 mm $\text{Me}_7\text{Si}_3\text{H}$; hence 40 mm Me_3SiH gave 2.7 mm $\text{Me}_5\text{Si}_2\text{H}$, while 2.7 mm $\text{Me}_5\text{Si}_2\text{H}$ gave 0.6 mm $\text{Me}_7\text{Si}_3\text{H}$, from which $k_6/k_5 \sim 3.3$.

2. Photolysis of $(\text{Me}_2\text{Si})_6$ in the presence of "pentamethyldisilane"

The main reactions here were also silylene insertions, initiation by reaction 4 being followed by reactions 6 and 10, the latter resulting from the presence of ca. 11% of $\text{HMe}_2\text{SiSiMe}_2\text{H}$ as an impurity in the $\text{Me}_5\text{Si}_2\text{H}$. There were also minor reactions involving $\text{Me}_2\dot{\text{S}}\text{iH}$ and $\text{Me}_3\text{Si}\cdot$ radicals. Again, as in Table 1, yields in

Table 2 were temperature-independent and similar steady state considerations apply, whence $E_3 = E_6 = E_{10}$. Hence $E_3 = E_5 = E_6 = E_{10}$, and considering the nature of reaction 3 and the close equality of E_3 , E_5 , E_6 and E_{10} , it is very likely that all of these activation energies are approximately zero. Comparison of the mean values for reaction 5 in Table 1 and for reaction 6 in Table 2 leads to $k_6/k_5 \sim 2.8$, in reasonable agreement with the earlier estimate of 3.3. Similarly, from Table 2, $k_{10}/k_6 \sim 1.4$. Hence $k_5 : k_6 : k_{10} \sim 1 : 3.1 : 4.3$.

The mechanism of pyrolysis of $\text{Me}_5\text{Si}_2\text{H}$ can now be considered further in the light of the above results. A reasonable scheme:



The kinetic characteristics of this scheme were studied by computer-aided numerical integration [7]. With k_{-5} equal to the experimental value [1] and reasonable estimates of k_5 and k_6 such that $k_6 = 3.1 \times k_5$ (with $E_5 = E_6 = 0$), values of k_{-6} and k_3 were adjusted until the computed progress curves for the decomposition of pentamethyldisilane agreed with experiment [1]. Whilst unique estimates of these rate constants are not yet possible, sensible values which gave excellent agreement with experiment over the temperature range are in Table 4. This agreement was destroyed when $E_5 = E_6 \geq 5 \text{ kJ mol}^{-1}$.

These figures confirm that heptamethyltrisilane is less stable thermally than pentamethyldisilane (the computed yield of heptamethyltrisilane is negligible, in keeping with experiment [1]), and confirm that the kinetics of the thermolysis of pentamethyldisilane are consistent with the results of this work for reactions 5 and 6. The temperature-dependence of the linearity of the experimental first order plots in the thermolysis [1] simply arises because k_{-5} increases relative to the other rate constants as the temperature is raised, hence maintaining first order behaviour to higher percentage decomposition.

3. Photolysis of $(\text{Me}_2\text{Si})_6$ in the presence of hydrogen chloride

Although the main product in these experiments was the dimethylsilylene insertion product, Me_2SiHCl , this might have been formed by a radical sequence in view of the predominance of radical reactions in the experiments with chlorosilanes. However, a radical mechanism for formation of Me_2SiHCl would produce equivalent quantities of hydrogen ($\text{Me}_2\dot{\text{S}}\text{iH} + \text{HCl} \rightarrow \text{Me}_2\text{SiHCl} + \text{H}\cdot$, followed by $\text{H}\cdot + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$). Since no significant amount of hydrogen was found, we conclude that the radical route was unimportant, and that Me_2SiHCl

TABLE 4

ARRHENIUS PARAMETERS FOR SIMULATING THE PYROLYSIS OF PENTAMETHYLDISILANE ^a

Reaction	-5	5	6	-6	3
$\log_{10} A$	12.93	9.0	9.5	13.0	5.0
$E \text{ (kJ mol}^{-1}\text{)}$	198	0	0	150	0

^a First order A factors are in s^{-1} and second order are in $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

was indeed formed by silylene insertion:



As reaction 3 would also be expected to occur in competition with reaction 11, the temperature-dependence of reaction 11 is relative to that of reaction 3.

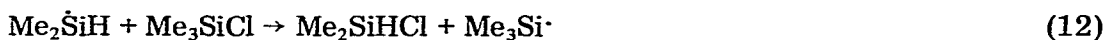
Assuming E_3 to be zero, E_{11} can then be calculated from the results in Table 3 between 423 and 478 K to be $27.7 \pm 1.0 \text{ kJ mol}^{-1}$.

4. Photolyses with methylchlorosilanes

In these experiments there was little or no evidence for silylene insertions. This might be because activation energies for insertion of dimethylsilylene into silicon-chlorine bonds are even higher than into hydrogen chloride, or because the main photochemical process in mixtures of $(\text{Me}_2\text{Si})_6$ with a chlorosilane is no longer the production of dimethylsilylene. Kumuda and coworkers [5] found that photolysis of $(\text{Me}_2\text{Si})_6$ in cyclohexane solution gave dimethylsilylene, which inserted readily into silicon-hydrogen or silicon-methoxy bonds. However, similar experiments with dimethyldichlorosilane proceeded quite differently, forming mainly higher molecular weight products containing several Me_2Si units. These results were explained in terms of a direct reaction of photochemically excited $(\text{Me}_2\text{Si})_6$ with the chlorosilane.

Our general impression of our experiments with $(\text{Me}_2\text{Si})_6$ and chlorosilanes is that little reaction occurred, and that such reaction as did take place mainly involved radicals. By analogy with the experiments in solution [5], it may be that in the gas phase chlorosilanes quench excited $(\text{Me}_2\text{Si})_6$, thus inhibiting its dissociation to give dimethylsilylene. Reasonable reactions leading to such products as were observed are as follows.

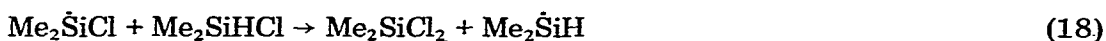
(i) $\text{Me}_3\text{SiCl} + (\text{Me}_2\text{Si})_6$. Main reactions, initiated by reaction 7:



Chlorine-abstraction from silicon chlorides by silyl radicals, as in reaction 12, is known to be rapid compared to hydrogen abstraction [8]. Minor reaction:



(ii) Me_2SiHCl . Main reactions:



Minor reactions:



Reaction 24 occurred to a very small extent, and the main source of HCl was probably not reaction 23, but simply some heterogeneous hydrolysis of Me_2SiHCl . A radical route to HCl is thermodynamically improbable.

(iii) $\text{Me}_2\text{SiHCl} + (\text{Me}_2\text{Si})_6$. The presence of $(\text{Me}_2\text{Si})_6$ caused a sharp drop in the yields of H_2 and CH_4 , i.e. in the rates of reactions 15 and 16, implying preferential absorption of light by $(\text{Me}_2\text{Si})_6$, or perhaps a quenching process. The main reactions were 7, followed by 21 and 18. Since reaction 4 also occurred to some extent, reaction 24 was more important than in the photolysis of Me_2SiHCl alone.

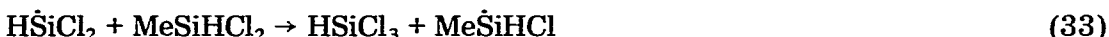
(iv) MeSiHCl_2 . In this case, the formation of a relatively large amount of HCl might be evidence for the primary silylene-forming reaction:



but there was no sign of the consequential insertion product:



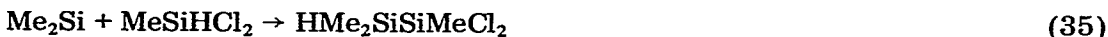
It is more likely that the HCl resulted from some hydrolysis of MeSiHCl_2 by adsorbed water in the apparatus. In keeping with this explanation there were some unidentified mass spectral peaks which could have come from siloxanes. The main reactions probably involved radicals:



(v) $\text{MeSiHCl}_2 + (\text{Me}_2\text{Si})_6$. The presence of $(\text{Me}_2\text{Si})_6$ reduced the rates of reactions 27 and 28, as it did in (iii) above. The main reactions were 7, followed by



then by 31, 30, and 22. A very minor sequence was reaction 4, followed by the insertion reaction:



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